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HIGH-PRESSURE OXYGEN LEACHING OF TIONITE RESIDUE FOR TITANIUM RECOVERY

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Abstract
Tionite is a solid residue formed during the production of titanium dioxide through the chloride process. This material is acidic and contains a high concentration of titanium, which makes it a potential secondary resource for titanium recovery. Instead of being disposed of as hazardous waste, tionite can be processed to extract valuable metals, particularly titanium. In this study, the recovery of titanium from tionite was carried out using an autoclave leaching method under high-pressure oxygen conditions. The presence of oxygen under pressure promotes the formation of titanium oxysulfate, which enhances the dissolution of titanium into solution. This approach enables selective leaching of titanium while limiting the dissolution of other unwanted elements. The leaching experiments were designed to explore optimal conditions for efficient titanium recovery, including temperature, pressure, and leaching time. The main objective of this research is to present a viable route for the valorisation of tionite by turning a hazardous acidic waste into a valuable source of titanium. This process contributes to waste reduction in the titanium dioxide industry and supports more sustainable resource management.

***Keywords**: titanium, high pressure leaching, hydrometallurgy, tionite, waste management*

1. INTRODUCTION

The chloride process (Figure 1), first commercialised by DuPont in the 1950s, has become the dominant method for producing high-purity titanium dioxide (TiO_2) pigments. Compared to the traditional sulfate process, it offers advantages in terms of energy efficiency, product quality, and waste management. This method typically utilises high-grade titanium-bearing raw materials such as rutile, synthetic rutile, and ilmenite, which are chlorinated in a fluidised bed reactor at elevated temperatures to produce titanium tetrachloride ($TiCl_4$). After purification, $TiCl_4$ is oxidised to form TiO_2, while chlorine is recovered and recycled. Despite its industrial advantages, the chloride process generates solid acidic residues and waste streams that require careful handling [1, 2].

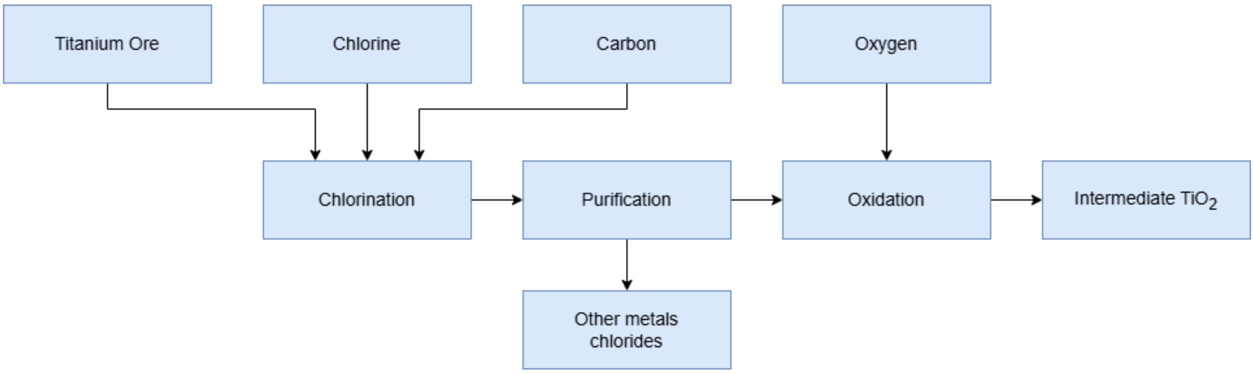

Figure 1. Flowsheet of chlorine process [3]

One such residue is tionite, a residue rich in titanium compounds, formed from unreacted ore, coke, and metal chlorides that are not volatilized during chlorination. Tionite is typically neutralised and landfilled, but its high titanium content makes it an attractive candidate for recovery and reuse. Utilising tionite for titanium extraction not only reduces environmental burdens associated with its disposal but also supports circular economy strategies within the titanium industry [4–6].

Several approaches have been explored for the valorisation of tionite, including pyrometallurgical and hydrometallurgical routes. Among them, hydrometallurgical methods such as acid leaching offer a selective and potentially scalable pathway for dissolving titanium into a recoverable form. Titanium can be leached as titanium oxysulfate in acidic media under oxidative conditions, and subsequently recovered through precipitation or solvent extraction. However, research on oxidative autoclave leaching of tionite under high-pressure oxygen remains limited [7–11].

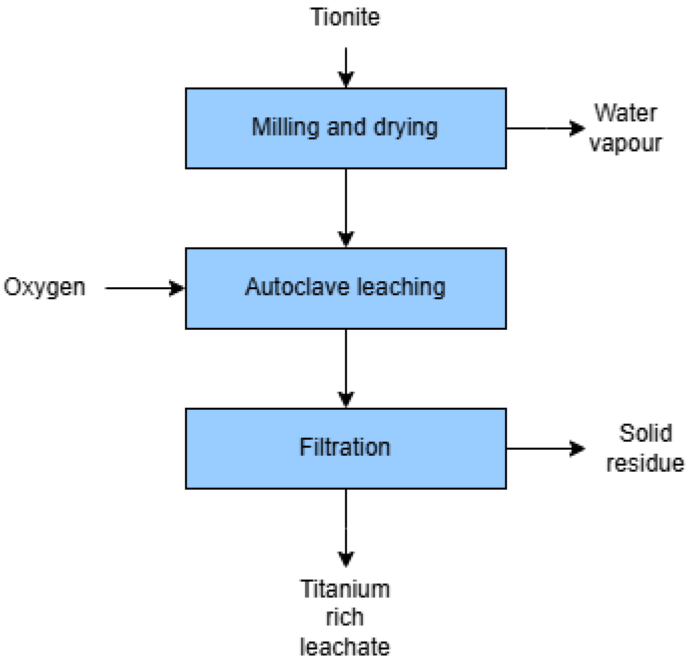

Figure 2. "State of the art" tionite processing

This study investigates the use of high-pressure oxygen in autoclave leaching to promote selective titanium dissolution from tionite, aiming to produce a titanium-rich solution suitable for further processing (Figure 1). The goal is to demonstrate a feasible and sustainable method for transforming hazardous industrial waste into a valuable resource, contributing to both environmental protection and material efficiency in titanium production.

2. EXPERIMENTAL

2.1 Methods

The mineralogical composition of the tionite was investigated using X-ray diffraction (XRD). Analyses were carried out at ambient conditions using a Rigaku Ultima IV diffractometer equipped with CuKα radiation. Operational parameters included a generator voltage of 40 kV, current of 40 mA, and a scan range of 10° to 100° 2θ, at a step size of 0.02° and scan speed of 1°/min. A D/TeX Ultra detector was employed in continuous scan mode. Samples were prepared on glass holders, and phase identification was performed using PDXL2 software (v2.8.4.0) in conjunction with the ICDD powder diffraction database.

The morphological and microstructural features of tionite, both before and after leaching, were examined using scanning electron microscopy (SEM). A Quattro S microscope (Thermo Fisher Scientific, USA) was operated in high vacuum mode at accelerating voltages between 5 and 20 kV. Energy-dispersive X-ray spectroscopy (EDS) was used alongside SEM to determine the elemental distribution across the sample surfaces, with a focus on titanium and associated elements.

The elemental concentrations in both solid samples and leachates were quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES), performed on a Spectro Genesis system. This technique enabled precise multi-element detection across a wide atomic mass range.

Leaching experiments

Titanium extraction experiments were conducted using a Büchi high-pressure autoclave (1.53 L capacity), engineered specifically for acidic leaching operations. The unit supports a maximum operating pressure of 200 bar and temperature up to 270 °C. The autoclave was operated with sulfuric acid as the leaching medium and oxygen overpressure (6–9 bar) to facilitate oxidative dissolution of titanium. Total system pressure ranged from 12 to 15 bar, accounting for both oxygen and steam.

The system features include a thermostatically controlled heat exchanger, mechanical stirring, real-time pressure and temperature monitoring (via manometer and digital probes), and sampling capability during operation. Heating was applied at a controlled rate of 10 °C per minute, and cooling was performed using an integrated chiller unit. Each experiment began with a manual sealing procedure and pressure integrity check.

2.2 Materials

In this study, tionite, a solid residue generated from the chloride-route titanium dioxide production process, was sourced from Venator GmbH. The raw material was initially dried and milled to achieve a uniform powder suitable for subsequent characterisation and processing.

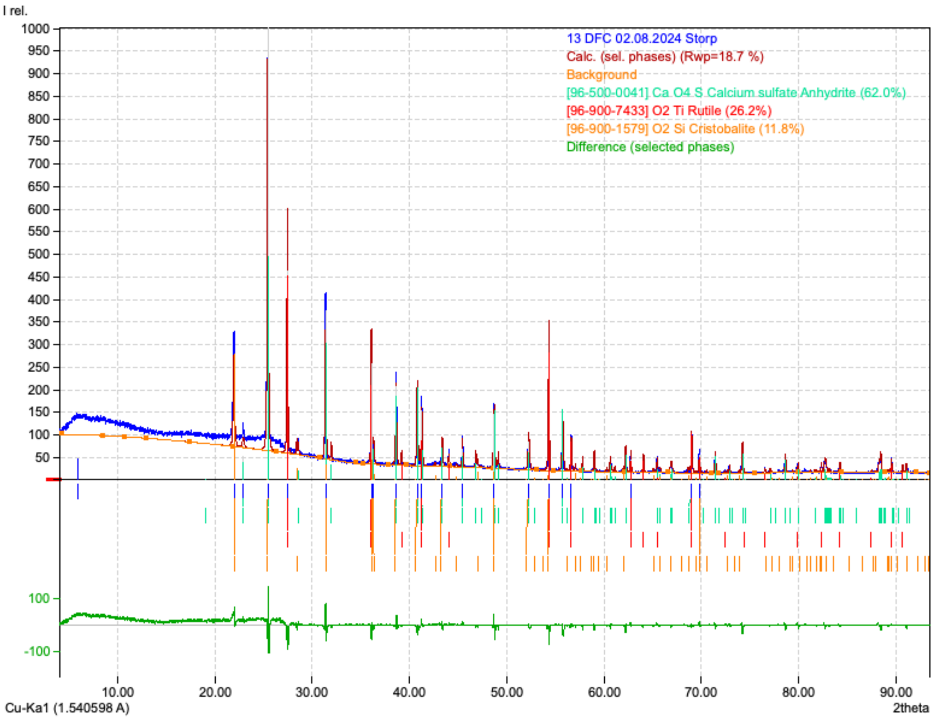

Figure 3. XRD analysis of tionite

The X-ray diffraction (XRD) analysis of the tionite sample revealed a complex multiphase composition, as shown in the diffractogram. The dominant crystalline phase identified in the sample is anhydrite ($CaSO_4$), comprising approximately 62.0 wt%. This phase is characteristic of residues resulting from sulfate-rich neutralisation processes in titanium dioxide production. Rutile (TiO_2), accounting for 26.2 wt%, is the principal titanium-bearing phase, confirming the potential of tionite as a source for titanium recovery through selective leaching. A minor phase, cristobalite (SiO_2), was also detected at 11.8 wt%, likely originating from inert siliceous components that remain unreacted during chlorination. The combination of these phases reflects the mineralogical complexity of tionite and supports its evaluation as a candidate for further hydrometallurgical processing.

Table 1. Tionite elemental composition

Material	Ti	Si	Al	Fe	Ca
Tionite	13.86 %	1.76 %	2.57 %	10.64 %	32 %

Based on the provided elemental composition from ICP analysis, it is evident that the results support the findings from the XRD analysis.

The high calcium content (32%) aligns well with the dominant presence of anhydrite ($CaSO_4$) identified by XRD, confirming that calcium is primarily present in the form of calcium sulfate. The significant titanium concentration (13.86%) corresponds to the rutile (TiO_2) phase detected in the diffraction pattern, validating that titanium is present in a crystalline, leachable form. Additionally, the presence of silicon (1.76%) is consistent with the identification of cristobalite (SiO_2), although it appears in a lesser amount both chemically and mineralogically. Aluminium and iron, though not directly observed as major crystalline phases in the XRD pattern, are present in considerable quantities (2.57% and 10.64% respectively), likely occurring in amorphous or minor crystalline phases not resolved in the diffractogram.

Table 2. Design of leaching experiments

Exp No.	Temperature (°C)	Pressure (bar)	Concentration of acid (mol/dm^3)	Time (min)
1	150	6	2,5	60
2	150	6	5	120
3	180	6	5	120
4	150	9	5	120
5	150	9	5	60

The leaching experiments were conducted at the Institute of Metallurgy and Metal Recycling (IME), RWTH Aachen University, to investigate the effect of various parameters on titanium recovery from tionite. A total of five experiments were performed in a controlled autoclave environment. In all experiments, a solid-to-liquid ratio of 1:10 was maintained, and continuous mixing was ensured at a speed of 500 RPM to promote homogeneous reaction conditions. This experimental design allowed for the evaluation of the influence of individual and combined parameters on the leaching efficiency and titanium dissolution behaviour.

3. RESULTS AND DISCUSSION

Leaching has been done using sulfuric acid. After the experiments, ICP analysis has been done, and the leaching efficiency calculated (Figure 4).

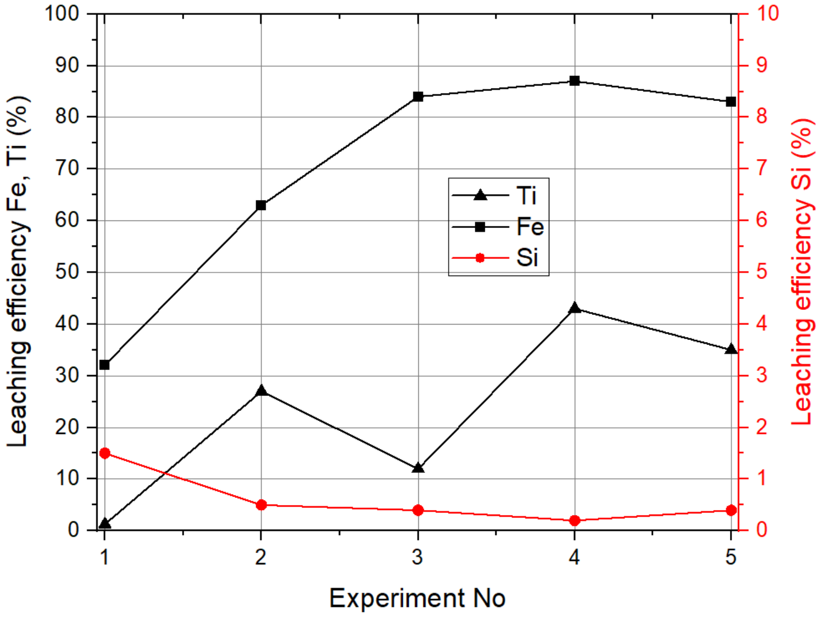

Figure 4. Leaching efficiency for different elements

The leaching efficiency results demonstrate varying behaviours of titanium (Ti), iron (Fe), and silicon (Si) under different experimental conditions. Titanium shows a gradual increase in leaching efficiency across the experiments, with the highest value around 43% achieved in Experiment 4, conducted at 150 °C, 9 bar oxygen pressure, 5 mol/dm^3 sulfuric acid concentration, and 120 minutes of leaching time. This suggests that higher oxygen pressure and acid concentration significantly enhance titanium dissolution.

However, the maximum titanium recovery remains relatively low. This limited leachability, despite aggressive conditions, indicates that the primary titanium-bearing phase (rutile) is highly resistant to dissolution. Rutile's compact and stable crystalline structure makes it difficult to break down under typical hydrometallurgical conditions, even in an oxidising and acidic environment.

Iron shows fluctuating leaching behaviour, with its highest efficiency (~88%) in Experiment 4. The lower and less predictable dissolution of iron may be influenced by secondary phase stability or partial passivation during leaching. Silicon consistently exhibits very low leaching efficiency (below 2%), reflecting its low solubility under the experimental conditions and suggesting prevention of silica gel formation.

Overall, the results confirm that while titanium can be partially recovered through high-pressure oxygen leaching, the process is hindered by the refractory nature of rutile. Future improvements may require additional pretreatment steps to disrupt the rutile structure or alternative leaching strategies to enhance titanium recovery.

SEM analysis coupled with EDS of solid residue from experiment 4 has confirmed leaching results (Figure 5).

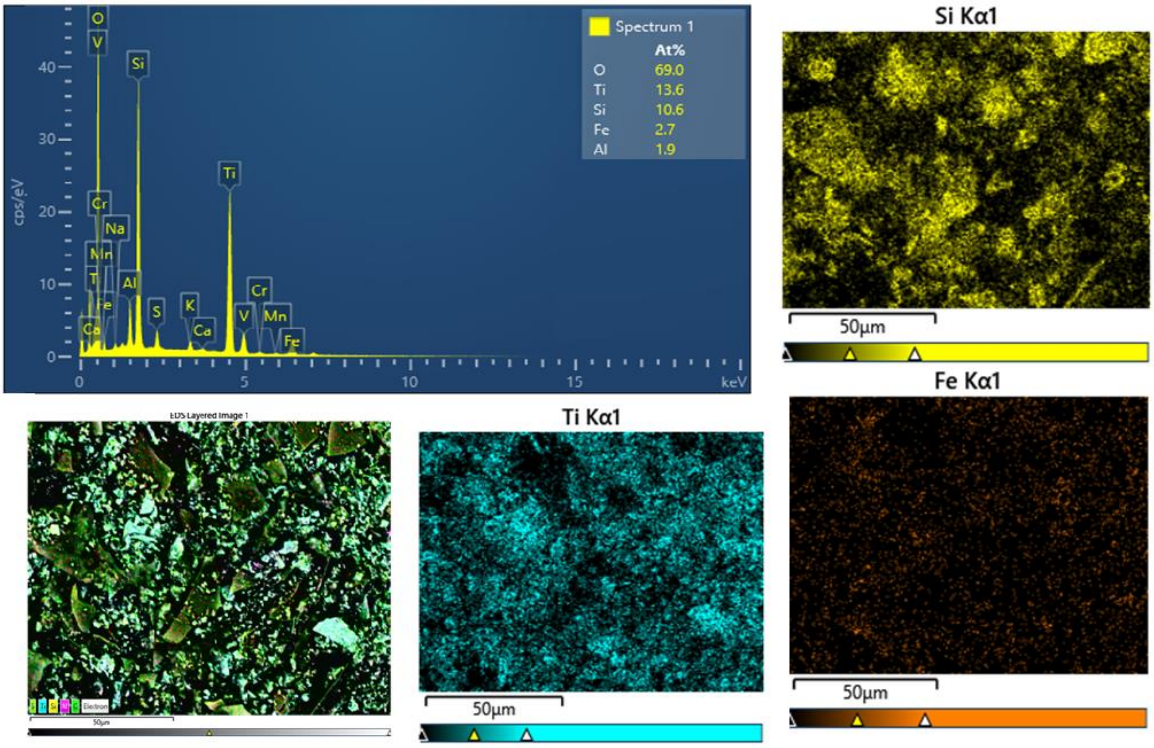

Figure 5. SEM-EDS analysis of solid residue from experiment 4

The SEM-EDS analysis of the solid residue from Experiment 4 provides additional insights into the elemental distribution and confirms the observed leaching efficiencies. The EDS spectrum (top left) shows dominant peaks for oxygen and titanium, with a measured atomic percentage of 13.6% Ti and 10.6% Si, while iron is present at only 2.7%. This aligns well with the quantitative leaching results, where iron exhibited the highest leaching efficiency, confirming its effective removal from the solid matrix.

The element mapping images support these findings:

- The Fe Kα1 map shows a very faint and sparse distribution of iron, indicating that most of the iron was successfully leached from the solid during high-pressure oxygen leaching.
- The Ti Kα1 and Si Kα1 maps reveal a dense and uniform presence of titanium and silicon, respectively, across the entire residue surface. This suggests that a significant portion of both elements remains in the solid phase, reflecting only modest titanium leaching (~40% at best conditions) and poor silicon leaching (under 2%).

These results confirm that titanium, present largely in the rutile phase (as shown in the XRD analysis), exhibits structural resistance to dissolution under the tested leaching conditions. Silicon, likely present as cristobalite, also shows limited reactivity, remaining in the residue in high amounts. In contrast, iron appears to be present in more soluble phases, explaining its near-complete extraction under optimised conditions.

4. CONCLUSIONS

The conducted leaching experiments using sulfuric acid under varying temperature, pressure, and acid concentration conditions demonstrated distinct behaviours for iron, titanium, and silicon recovery from tionite. The process proved highly effective for iron extraction, achieving a maximum leaching efficiency of approximately 88% under optimized conditions (150°C, 9 bar oxygen, 5 mol/dm³ H2SO4, 120 min). This high iron recovery indicates that iron-bearing phases in the material are readily soluble under the applied oxidative acidic environment.

Titanium exhibited moderate leaching performance, with a maximum recovery of approximately 43% under the same experimental conditions. The limited leachability of titanium is attributed to its presence primarily in the rutile phase, a highly stable and refractory mineral. The strong crystalline structure of rutile resists leaching, even under elevated temperature and pressure, highlighting the need for alternative or additional treatment methods to improve Ti recovery.

Silicon leaching remained consistently low across all tests, with efficiencies below 2%. This minimal dissolution suggests that silica remains largely in the solid phase, likely in the form of cristobalite, and does not form problematic silica gel during leaching. The absence of gel formation is a favourable outcome, simplifying solid-liquid separation and downstream processing.

Overall, the study confirms that high-pressure oxygen leaching is a promising method for efficient iron removal from tionite. However, due to the refractory nature of rutile, future research will focus on enhancing titanium recovery, potentially through pretreatment strategies or alternative leaching systems to improve titanium extraction.

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